IV.B.9 Montana PEM Membrane Degradation Study, Year 1 Report*

Dan Stevenson
CTA
1500 Poly Drive, PO Box 1439
Billings, MT 59103
Phone: (406) 248-7455; E-mail: dans@ctagroup.com

Lee H. Spangler (Primary Contact)
Montana State University
207 Montana Hall
Bozeman, MT 59717
Phone: (406) 994-2891; E-mail: spangler@montana.edu

DOE Technology Development Manager: Amy Manheim
Phone: (202) 586-1507; Fax: (202) 586-9811; E-mail: Amy.Manheim@ee.doe.gov

**Congressionally directed project*

Objectives

- Develop a system capable of measuring current and voltage performance for each membrane in a polymer electrolyte membrane (PEM) fuel cell stack and record the performance of each individual cell.
- Develop a single-cell PEM fuel cell to allow *in situ* synchrotron x-ray measurements of the cell in operation.
- Perform initial magnetic resonance microimaging experiments on membrane materials.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- E. Durability (distributed generation)
- G. Power Electronics
- P. Durability (components)

Approach

- Design a system to capture individual cell performance in real time (current, voltage, temperature points taken every 0.5 milliseconds).
- Test the stack response as it is subjected to load transients. Monitor each cell in the stack for its entire lifetime.
- As failures occur, analyze the cell using x-ray techniques, including methods that provide spatial resolution and chemical composition information.
- As failures occur, analyze the membrane material using magnetic resonance imaging (MRI) microimaging technique to get information about membrane permeability.
- Search electrical records of failed membranes to see if mode of failure or an electrical signature of failure can be discerned.

Accomplishments

- Fully instrumented two separate 80-membrane PEM fuel cells.
- Performed initial test runs to debug hardware and software in preparation for long-term testing.
- Performed initial x-ray analysis on degraded membranes.
- Concluding study reproducing bulk nuclear magnetic resonance (NMR) study of Nafion 117 solvent mobility dependence on methanol (MeOH) concentration; manuscript preparation in progress.
- Initiating MRI studies of PEMs after failure during fuel cell operation by other components of project.
- Initiating combined sequential MRI and x-ray analysis of membranes.

Future Directions

- Operate instrumented fuel cells under load transients and determine performance degradation of cells.
- Construct electrophoretic NMR probe with M. Holz visiting Montana State University (MSU) during summer or fall.
- Perform combined sequential MRI and x-ray analysis of membranes.

Introduction

The Montana State University PEM Membrane Degradation project is geared towards determining how and why membranes in fuel cells degrade and fail. By monitoring every individual membrane in a fuel cell 2000 times/sec while the cell is subjected to real-world type use, we hope to 1) cause the types of degradation users see, but in a controlled environment; 2) determine an electrical signature that will identify what causes failure, or at least warns of impending failure; 3) perform advanced x-ray and MRI characterization of the degraded membranes to provide information that may result in improvements of the membrane material; and 4) perhaps allow design of electronic control systems that will prevent fuel cells from operating under conditions where damage is likely to occur.

Approach

The Montana State University PEM Membrane Degradation project has three interdependent components: 1) fuel cell electrical characteristics monitoring, 2) synchrotron-based x-ray characterization of membranes, and 3) NMR microscopy of polymer electrolyte membranes. The project will involve continuous, comprehensive monitoring of PEM fuel cell electrical performance while the cell is being subjected to real-world types of loads and transients. A fuel cell enclosure will contain 80 membranes housed in 8 cartridges. Each side of the cartridge (5 membranes) will contain an analog to digital (A/D) converter that will measure voltage for each individual membrane, current and temperature at a 2000 Hz rate. This total of 224,000 data points per second will be stored to provide a permanent record of performance of each individual membrane over its entire life span. This comprehensive set of data has promise of yielding an electrical signature of impending failure. Membranes in various states of degradation and failure will be extracted for characterization using the two analytical techniques in the project.

X-ray characterization will be used to investigate the catalyst, and possible poisoning of the catalyst, via x-ray photoelectron spectroscopy. In addition, a synchrotron-compatible fuel cell has been constructed to perform measurements during operation. If the electrical monitoring program identifies load conditions that generate degradation, *in situ* measurements can be performed under these conditions to determine chemical changes in the catalyst, and possibly in the membrane material itself. These measurements can be performed with 10 μm or better spatial resolution so localized effects and spreading of damage can be studied, which may provide insight into the mechanism of failures. NMR microimaging techniques will also be utilized to investigate membrane performance. Rather than imaging the membrane itself, this technique will provide images that contain information about water and hydronium ion mobility within the membranes. These imaging experiments will be performed on membranes in various states of degradation.

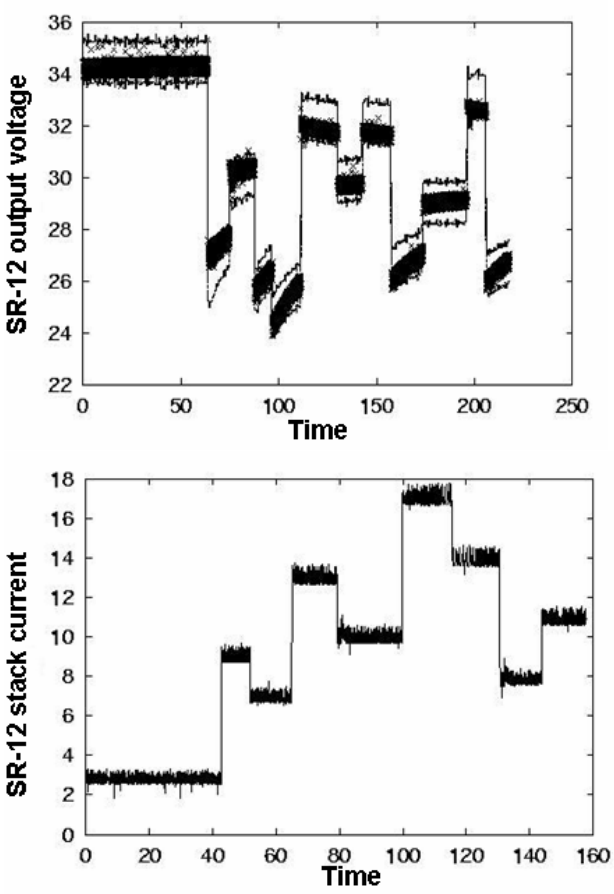

Figure 1. Cross validation of predicted fuel cell output voltage (dark line is the predicted response). Dynamic models are needed for design of multi-source and distributed power systems that incorporate fuel cells to ensure good system performance and prevent degradation.

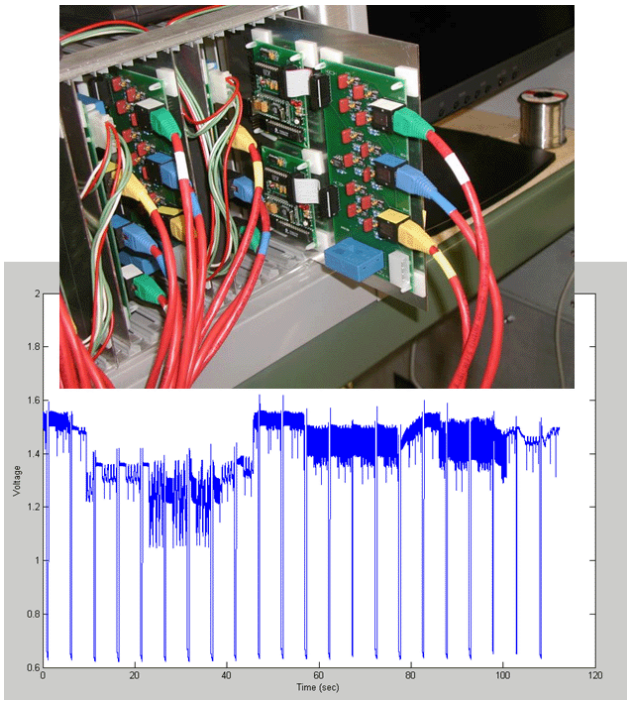

Figure 2. Example of high resolution temporal data acquired from system. Spikes are due to fuel cell system switching membranes on & off.

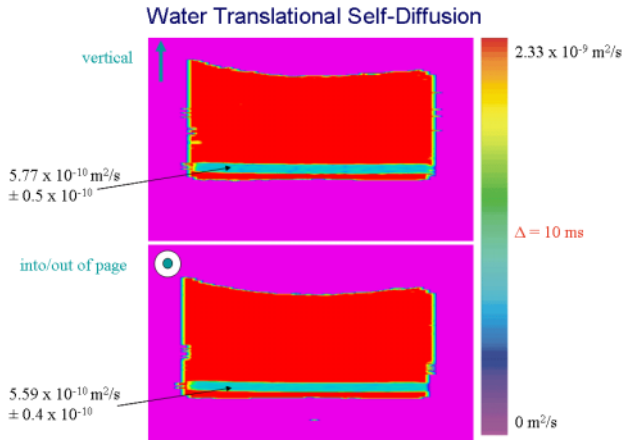

Figure 3. Spatially-resolved data on proton mobility using T1 and T2 magnetic relaxation and molecular self-diffusion as a function of membrane depth have reproduced bulk NMR measurements from literature with spatial resolution under liquid saturated conditions and as a function of MeOH concentration.

Results

The fuel cell enclosures are fully instrumented and operating with programmable loads to simulate real-world transients. Additionally, a dynamic terminal model has been developed to permit accurate modeling of the fuel cell electrical response (Figure 1). Preliminary data shows the high temporal resolution attained by the home-built data acquisition system (Figure 2). The data shown are for a single cell within the 80-cell enclosure. The zero-going spikes are the result of the manufacturer's control system intentionally shutting down cells temporarily and alternately, perhaps as a hydration control measure.

Preliminary images of Dupont Nafion117 PEMs have been acquired. While *bulk* NMR measurements of electroosmotic mobility[1] and molecular self-diffusion of water[2] within PEMs have been reported, to our knowledge, the images generated by this project are the first *spatially*-resolved *images* of

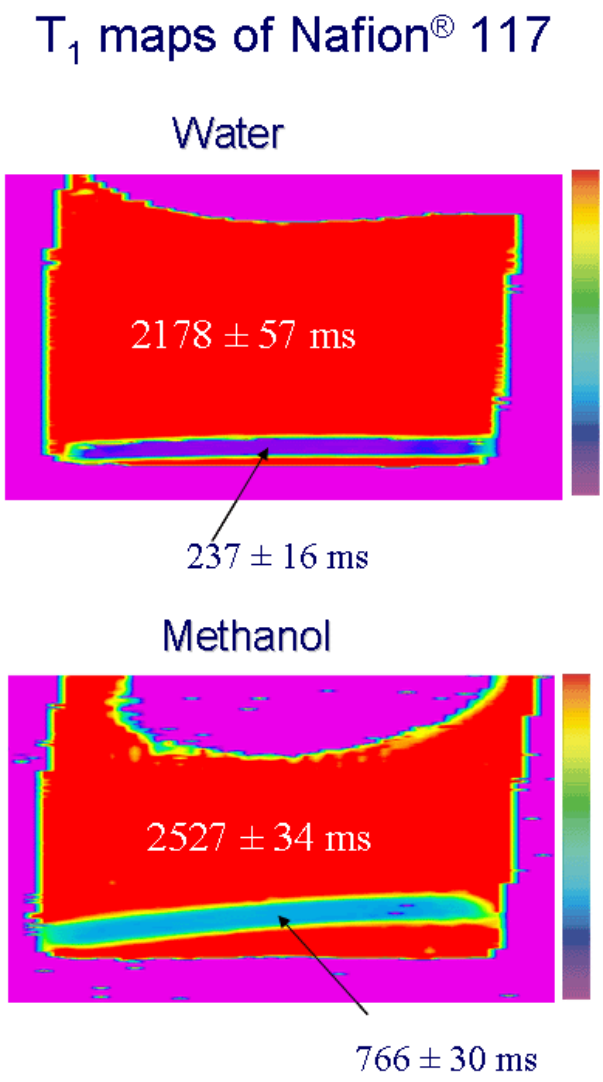

Figure 4. T1 Relaxation Times for Nafion 117 in Water and Methanol (Note PEM swelling and increased mobility of MeOH relative to H_2O.)

water within a PEM. Figure 3 shows spatially-resolved data on proton mobility using T1 and T2 magnetic relaxation and molecular self-diffusion as a function of membrane depth with spatial resolution under liquid saturated conditions and as a function of MeOH concentration. The relaxations measured are in excellent agreement with bulk NMR measurements from literature [3]. Figure 4 compares T1 relaxation times for Nafion 117 in water and methanol. NMR imaging allows measurement of both relaxation and of changes in polymer dimension. Swelling of the membrane is quite evident in the membrane immersed in methanol.

Conclusions

The three-pronged approach shows promise for yielding insights to degradation mechanisms and the changes in materials properties that result.

References

1. M. Ise, K.D. Kreuer, and J. Maier, Electroosmotic drag in polymer electrolyte membranes: an electrophoretic NMR study. *Solid State Ionics*. **125**: 213 (1999).

2. S. Hietala, S.L. Maunu, and F. Sundholm, Sorption and diffusion of methanol and water in PVDF-g-PSSA and Nafion 117 polymer electrolyte membranes. *Journal of Polymer Science: Part B: Polymer Physics*. **38**: 3277 (2000).

3. S. Hietala, S.L. Maunu and F. Sundholm, *J. Polym. Sci. B Polym. Phys.* **38** 3277 (2000); B. MacMillan, A.R. Sharp and R.L. Armstrong, *Polymer.* **40** 2471 (1999).

FY 2004 Publications/Presentations

1. S.R. Shaw, "Instrumentation for PEM Fuel Cell Transient Degradation Monitoring," Proceedings of the 2004 IEEE PES General Meeting in Denver, CO, June 5-11.

2. J.D. Seymour, S.L. Codd, J.C. Mabry, S.C. Busse and E.S. Peterson, "NMR Microscopy of Water and Methanol Distribution and Dynamics in Polymer Electrolyte Membranes," North American Membrane Society, 14th Annual Meeting, Jackson Hole, WY, May 17-21, 2003.

3. J.C. Mabry, S.L. Codd, S.C Busse, and J.D. Seymour, "MR Microscopy of Water Distribution and Dynamics in Polymer Electrolyte Membranes (PEMs)," 7th International Conference on Magnetic Resonance Microscopy, Snowbird, UT, September 21-25, 2003.

4. Invited panelist at for the technical session on fuel cell technology at the 2004 IEEE PES general meeting.